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<b>(21) International Application Number:</b> PCT/GB92/01200 <b>(22) International Filing Date:</b> 2 July 1992 (02.07.92)  <b>(30) Priority data:</b> 9114323.0 2 July 1991 (02.07.91) GB 9118163.6 22 August 1991 (22.08.91) GB  <b>(71) Applicant (for all designated States except US):</b> UNIVERSITY OF WARWICK [GB/GB]; Gibbet Hill Road, Coventry CV4 7AL (GB).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> BHATTACHARYA, Ashok, Kumar [IN/GB]; Department of Engineering, University of Warwick, Gibbet Hill Road, Coventry CV4 7AL (GB).		<b>(74) Agent:</b> BANNERMAN, D., G.; Withers & Rogers, 4 Dyer's Buildings, Holborn, London EC1N 2JT (GB).  <b>(81) Designated States:</b> US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CATALYSTS FOR THE PRODUCTION OF CARBON MONOXIDE  <b>(57) Abstract</b>  A method of partially oxidising methane to carbon monoxide comprises contacting oxygen and excess methane with a catalyst comprising a platinum group metal and/or metal oxide supported on a lanthanide oxide, and/or an oxide of a metal from group IIIA and/or an oxide from a metal from group IVA of the Periodic Table and/or alumina. The platinum-group metal is preferably palladium, others are platinum, rhodium and iridium. One preferred lanthanide oxide is cerium oxide, one preferred oxide of a metal from group IIA of the Periodic Table is yttrium oxide and one preferred oxide of a metal from group IVA of the Periodic Table is zirconium oxide.		

## CATALYSTS FOR THE PRODUCTION OF CARBON MONOXIDE

This invention concerns a process for the partial catalytic oxidation of methane to carbon monoxide and either hydrogen or steam or a mixture of hydrogen and steam.

Carbon monoxide is a very useful material for organic synthesis. Methane is widely available from natural gas deposits, but until now no practical catalytic method has been known for the partial oxidation of methane to carbon monoxide. Complete oxidation of methane of course yields carbon dioxide.

According to this invention, a method of oxidising methane to carbon monoxide and either hydrogen or steam or a mixture of hydrogen and steam comprises contacting oxygen and excess methane with a catalyst comprising a platinum group metal and/or metal oxide supported on a lanthanide oxide, and/or an oxide of a metal from group IIIA and/or an oxide from a metal from group IVA of the Periodic Table and/or alumina. The platinum-group metal is preferably palladium, others are platinum, rhodium and iridium. One preferred lanthanide oxide is cerium oxide, one preferred oxide of a metal from group IIIA of the Periodic Table is yttrium oxide and one preferred oxide of a metal from group IVA of the Periodic Table is zirconium oxide.

Mixed oxides of general formula  $ABO_3$  where A is an alkaline earth metal and B is another metal such as Ti,

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Zr, Hf or Ce e.g. Ba may also be used, e.g.  $\text{BaCeO}_3$ ,  $\text{SrCeO}_3$ ,  $\text{BaZrO}_3$ ,  $\text{SrZrO}_3$  and  $\text{SrTiO}_3$ .

The reaction is preferably carried out at around  $750^\circ\text{C}$ . At temperatures of around  $500$ - $600^\circ\text{C}$  a mixture of CO and  $\text{CO}_2$  is obtained. At higher temperatures the proportion of CO increases and at lower temperatures the proportion of  $\text{CO}_2$  increases. In the case of  $\text{CeO}_2$  almost no  $\text{CO}_2$  is produced at a temperature of  $750^\circ\text{C}$ . The proportion of hydrogen to steam produced increases with increasing temperature.

The palladium or other platinum group metal may preferably be deposited on an oxide as specified above and that metal oxide may, in turn, be coated onto any high surface area thermally-stable support, such as a ceramic material.

The invention will now be described in more detail by way of non-limiting example and with reference to the drawings, in which:

Fig.1 is a graph showing the amounts of CO and  $\text{CO}_2$  obtained from the oxidation of  $\text{CH}_4$  using  $\text{Pd/CeO}_2$  and  $\text{CeO}_2$  catalysts and various temperatures; and

Fig.2 is a graph showing the percentages of CO and  $\text{CO}_2$  at different space velocities using a  $\text{Pd/CeO}_2$  catalyst.

A thin layer of palladium metal was deposited on a number of catalyst supports. This was done by treating the supports with palladium nitrate and decomposing it by

heating to 550°C. The initial decomposition produces a mixture of palladium metal and oxide. This may be used as it is or may be reduced e.g. with hydrogen, to convert some or all of the oxide to the metal. The  $\text{CeO}_2$ ,  $\text{Y}_2\text{O}_3$  and  $\text{ZrO}_2$  supports used were obtained commercially from Johnson Matthey plc. The  $\text{TiO}_2$  was purchased from Tioxide Ltd.  $\text{Al}_2\text{O}_3$  was obtained commercially or prepared by standard preparative ceramic techniques or by the known hydroxide precipitation method.

The  $\text{BaCeO}_3$  and  $\text{SrCeO}_3$  were obtained by standard ceramic methods from commercially-available oxides (e.g. those supplied by Johnson Matthey plc) or from nitrates (also available from Johnson Matthey plc).

The resulting supported catalysts were then utilised to catalyse the reaction between excess methane and oxygen at 750°C.

The following Table shows the percentage of methane converted in the reaction, when carried out at a temperature of 750°C and a space velocity (GHSV) of 5000  $\text{hr}^{-1}$  using a feed gas comprising 45%  $\text{CH}_4$ , 5%  $\text{O}_2$ , 55% Av. The Table shows the percentage of both carbon monoxide and carbon dioxide in the converted proportion of methane. Carbon dioxide is generally an undesired by-product of the reaction. The results show that cerium oxide, yttrium oxide and zirconium oxide were particularly effective as catalyst supports in the production of carbon monoxide, giving both a reasonable

percentage conversion, and very high selectivity for CO vis-à-vis CO<sub>2</sub>. SiO<sub>2</sub> on the other hand, was particularly unsatisfactory. The use of SiO<sub>2</sub> is outside the scope of this invention.

TABLE

Catalytic activity of Pd supported on different oxides at 750°C, at GHSV of 5000 hr<sup>-1</sup> with a feed composition of 45% CH<sub>4</sub> : 5% O<sub>2</sub> : 55% Ar.

Support	Rate of Conversion of CH <sub>4</sub> ( $\mu$ mole s <sup>-1</sup> m <sup>-2</sup> )	% Selectivity	
		CO	CO <sub>2</sub>
Sc <sub>2</sub> O <sub>3</sub>	0.66	99.6	0.4
Y <sub>2</sub> O <sub>3</sub>	1.53	99.3	0.7
La <sub>2</sub> O <sub>3</sub>	0.44	99.5	0.5
TiO <sub>2</sub>	0.13	92.3	7.7
ZrO <sub>2</sub>	1.10	98.3	1.7
HfO <sub>2</sub>	1.56	99.3	0.7
CeO <sub>2</sub>	1.80	99.4	0.6
Sm <sub>2</sub> O <sub>3</sub>	0.74	58.8	41.2
Al <sub>2</sub> O <sub>3</sub>	0.90	99.5	0.5
SiO <sub>2</sub>	0.16	63.7	36.3
BaCeO <sub>3</sub>	0.45	51.0	48.0
SrCeO <sub>3</sub>	0.50	71.0	28.0

Fig. 1 is a graph comparing the yields of  $\text{CO}_2$  and CO obtained by utilising a variety of supports at different temperatures.

Fig. 1 shows clearly that as the temperature approaches  $750^\circ\text{C}$ , the amounts of  $\text{CO}_2$  and CO produced fall and rise respectively, for a supported Pd catalyst as specified in this invention (i.e. Pd/ $\text{CeO}_2$ ). The use of the  $\text{CeO}_2$  support alone as catalyst is shown by way of comparison only.

A mixture of CO,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{H}_2$  is useful as such in the synthesis of methanol and other alcohols.

Therefore, by careful selection of the catalyst and the temperature, a mixture of these four components can be obtained in such proportions that it may be used directly in alcohol synthesis.

Thus, according to another feature of the invention a process for the production of methanol comprises passing methane and oxygen over a catalyst as defined above at a temperature such that a mixture of CO,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_2$ , and possibly unreacted  $\text{CH}_4$  is obtained in appropriate proportions, and then passing said mixture over a methane synthesis catalyst.

The oxygen may be supplied as air and the methane synthesis catalyst may be a commercially available one e.g. a copper oxide/zinc oxide/alumina catalyst, such as that available from ICI.

Fig. 2 shows that the conversion to CO rather than

CO<sub>2</sub> is favoured by carrying out the reaction at higher space velocities.

As mentioned above, the catalyst layer was obtained by the decomposition of palladium nitrate. Other known methods can also be used (e.g. decomposition of palladium acetate or chloramines) involving different preparative techniques, and supports from different sources can also be employed having different physical properties. The method of deposition and the exact nature of the support affect both the conversion and the selectivity of the catalyst. Other factors which affect the performance of the catalyst are the space velocity (see Fig. 2), methane:oxygen ratio, and the partial pressures of methane and oxygen in the gas being treated.

CLAIMS

1. A method of oxidising methane to carbon monoxide and either hydrogen or steam or a mixture thereof characterised in that it comprises contacting oxygen and excess methane with a catalyst comprising a platinum-group metal and/or metal oxide supported on a lanthanide oxide and/or an oxide of a metal from group IIIA and/or an oxide of a metal from group IVA of the Periodic Table and/or alumina.
2. A method as claimed in claim 1, wherein the platinum-group metal is selected from palladium, platinum, rhodium and iridium.
3. A method as claimed in claim 2, wherein the platinum-group metal is palladium.
4. A method as claimed in any one of claims 1 to 3, wherein the lanthanide oxide is cerium oxide.
5. A method as claimed in any one of claims 1 to 4, wherein the oxide of a metal from group IIIA of the Periodic Table is yttrium oxide.



6. A method as claimed in any one of claims 1 to 5, wherein the metal from group IVA of the Periodic Table is zirconium oxide.

7. A method as claimed in claim 1, wherein the catalyst comprises a mixed oxide of general formula  $ABO_3$  where A is an alkaline earth metal and B is another metal.

8. A method as claimed in claim 7, wherein B is selected from titanium (Ti), zirconium (Zr), Hafnium (Hf) or cerium (Ce).

9. A method as claimed in any preceding claim, wherein the oxygen and methane is contacted with the catalyst at a temperature of  $750^{\circ}\text{C}$ .

10. A catalyst for oxidising methane to carbon monoxide comprising the catalyst defined in any one of claims 1 to 8.

FIG. 1

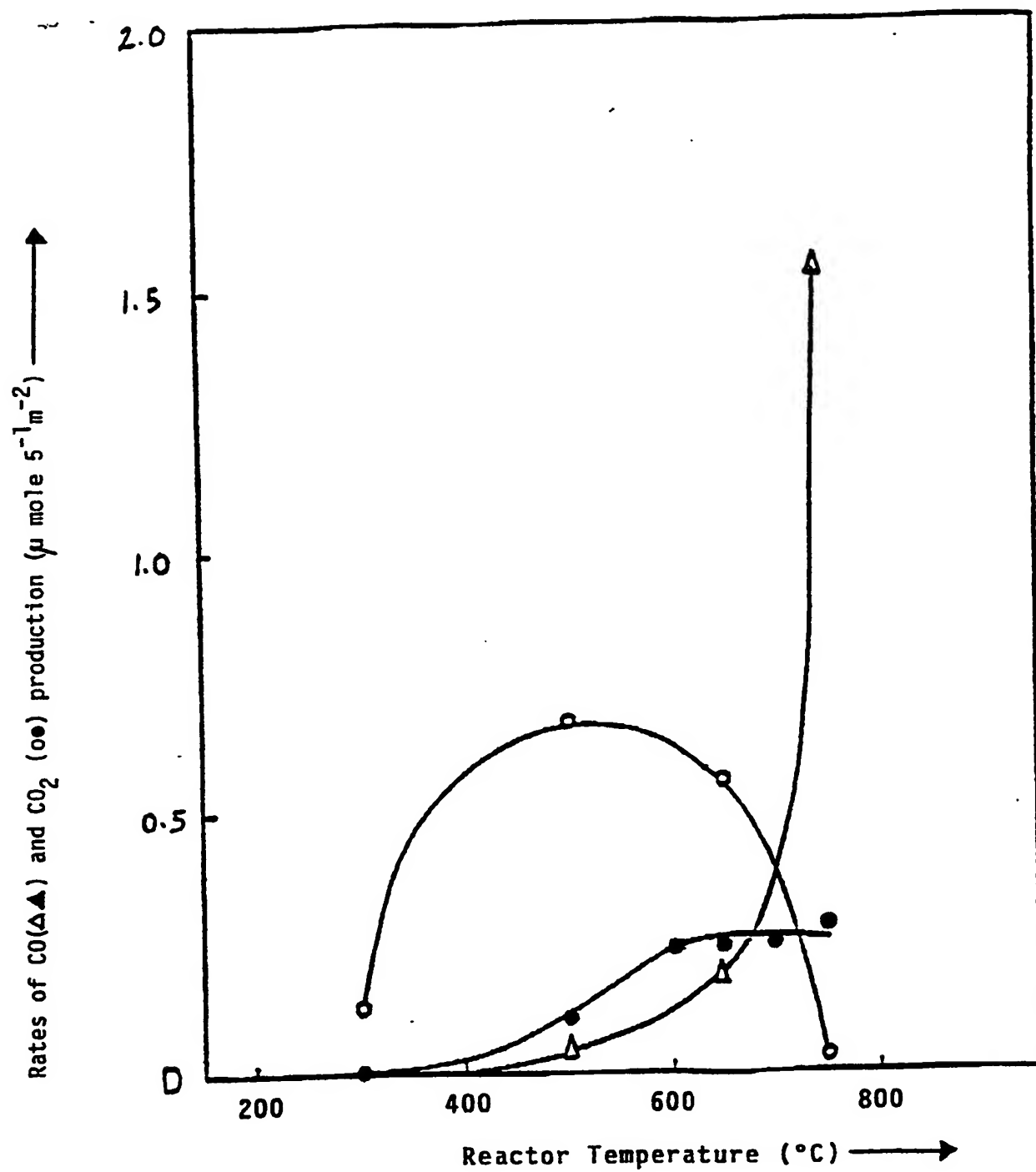


FIG. 2

